XP-001154423

PD: 1976 (10)
P: 192-201

REACTION OF WOOL KERATIN WITH EPOXIDES

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The addition reaction of various epoxides with wool fiber was investigated in the presence or absence of some salts in different solvents at 45 - 75°C. Tyrosine, cystine and basic amino acid residues of the keratin reacted even without salts while serine disappeared only in the presence of catalysts. The reaction rate varied with solvents used in the treatment and could be described by the solubility parameter of the solvent. The substituent effects of the epoxide on the add-ons were elucidated by the modified Taft equation.

INTRODUCTION

The literature contains some references to the epoxy-wool reactions: Fraenkel-Conrat and Olcott (1) have studied the reaction of wool with epichlorohydrin and ethylene and propylene oxide in aqueous buffered solutions. The reaction with glycidyl methacrylate in toluene has been investigated by Miller and Whitfield (2) in the presence of $AlCl_3$. Alexander and coworkers (3) have suggested the esterification of carboxylic groups of the peptide for the reaction. Zahn (4) has observed the decrease in the contents of histidine, lysine and cystine and the formation of cysteic acid during the epoxy reaction. Lennox (5) has found the homopolymerization of propylene oxide in keratin matrix, and suggested that amino and imino groups of the wool keratin react with monoepoxides and the crosslinking occurs in the reaction with epichlorohydrin. The wool-epoxide reaction, however, has been somewhat obscure.

Consequently, reactions of epoxides with protein fibers

have been under investigation in our laboratories for these years. The salt-catalyzed reaction of phenyl glycidyl ether with wool fabric has been subject of our previous report (6), in which the effects of various salts and solvents were preliminarily discussed. Histidine, lysine, arginie, serine, tyrosine and aspartic and glutamic acid have been also found to react with the epoxide. This paper is concerned with the study on the reactivity of some kinds of epoxides in various solvents, and discusses the effects of the epoxide and solvent on the reactivity of the reacting groups in wool keratin during the addition reaction of the epoxide.

EXPERIMENTAL

Materials

A Merino top, 67's quality, was extracted with benzene and ethyl alcohol in a Soxhlet apparatus for 9 hrs, and rinsed with ethyl alcohol and distilled water.

The epoxides were all of reagent grade, and used after distilled under reduced pressure. All of salt catalysts and solvents were of reagent grade, and were used without further purification.

Reaction Procedure

A 0.4 g fiber dried in a forced draft oven at 105°C for 45 min. was impregnated with the desired aqueous salt solution to an approximate 95% wet pickup. The loosely rolled top was then dropped into a graduated cylindrical flask containing 15 ml of a 1.43 M epoxide solution in various solvents; The flask was joined with a reflux condensor, held in a thermostatically controlled bath at the desired temperature, and occasionally shaken during the reaction time.

At the end of the reaction, the sample was washed with the solvent used and acetone, extracted with a boiling acetone for 30 min, and washed well with distilled water. The washed and air-dried fibers were dried in a oven at 105°C, placed in a desicator over the silica gel for 30 min, and weighed. The add-ons were determined from the weight increase of the fiber, a correction being made for the weight loss on treatment with

the salt alone.

Amino Acid Analysis

Dried wool fiber weighing about 200 mg, untreated or treated with epoxides, was hydrolyzed by heating for 8 hr at 105 - 108°C in 20 ml of aqueous 6 N HCl. The amino acid contents were determined on a buffered solution (pH 2.2) of the hydrolyzate (0.2 mg/0.1 ml) by using a JLC-5AH amino acid analyzer (JEOL Ltd.).

RESULTS AND DISCUSSION

The fibers padded with various concentrations of $Na_2S_2O_3$ in aqueous solution were treated with 1.43 M phenyl glycidyl ether solutions at 75°C for 3 hr. The results are given in Figure 1. The addition reaction proceeded successfully in these solutions as the epoxide reaction with *Philosamia Cynthia Ricini* silk fibroin (7) without the catalyst. The catalytic efficiency of the salt was not so much in wool keratin as in silk fibroin. This can be attributed partly to the participation of amino and

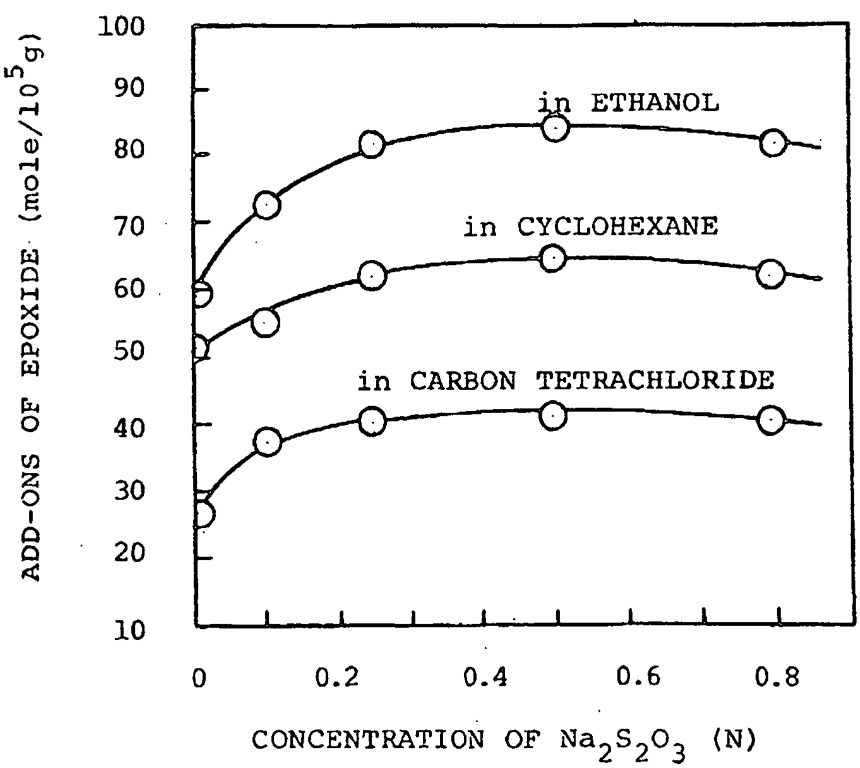

Figure 1: Concentration effect of $Na_2S_2O_3$ on the reaction of phenyl glycidyl ether and wool fiber at 75°C for 3 hr.

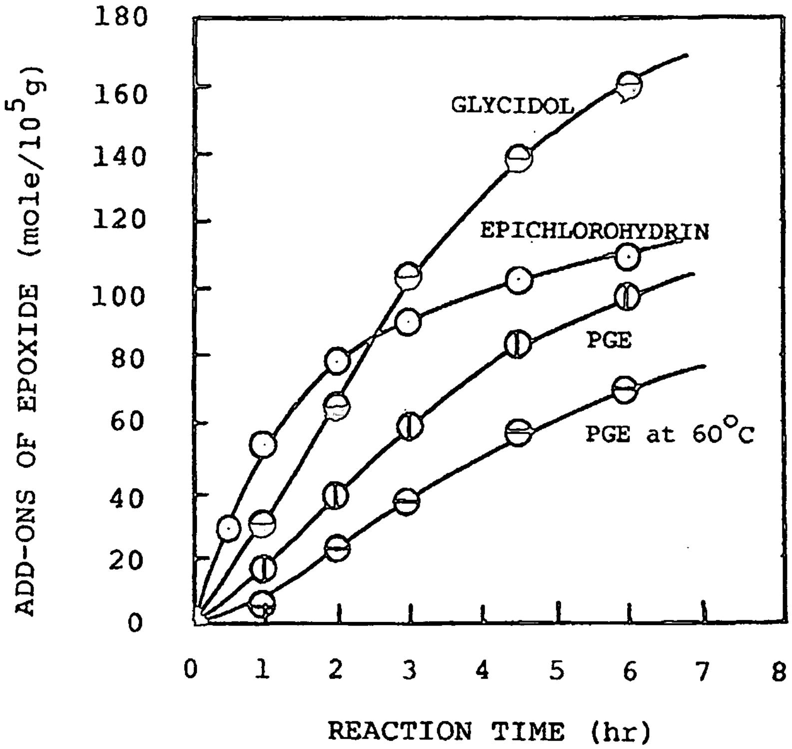

Figure 2: Time-conversion curves for the wool reaction with epoxides in ethanol at 68°C.

carboxylic groups, particularly histidine, lysine and aspartic and glutamic acid in the uncatalyzed reaction.

The time dependence of the reaction was investigated, and results are shown in Figure 2. The reaction of glycidol (G), epichlorohydrin (E) and glycidyl phenyl ether (PGE) was carried out with use of 0.25N $Na_2S_2O_3$ aqueous solution as a padding catalyst. The add-ons increased monotonously with time and were depended on the nature of the epoxide.

The solvents changed the reaction rates, as indicated by the data in Table 1, which shows the add-ons obtained by treating the fibers with 1.43 M PGE or E solutions in various solvents for 3 hr at 75 or 68°C without a padding catalyst. The dielectric constant of the solvent does not appear to give a clue to the reaction mechanism, unlike the case of homogeneous reaction of the epoxide in solutions (8). When the add-ons were plotted against the solubility parameters (9) of solvents a similar relationship was observed, as in the case of the silk

TABLE I

Solvent Effect on Wool Fiber Reaction with Epoxides

Solvent	Solubility Parameter (9)	Add-on (mole/10^5g)	
		PGE	E
n-Hexane	7.3	25.2	-
n-Octane	7.6	64.9	-
Lauryl alcohol	8.1	46.4	-
Cyclohexane	8.2	51.5	-
Methyl isobutyl ketone	8.4	17	-
n-Butyl acetate	8.5	21.2	-
Carbon tetrachloride	8.6	25.7	70.3
Toluene	8.9	25.9	67.7
Ethyl acetate	9.1	17.9	59.7
Benzene	9.2	18.7	-
Methyl ethyl ketone	9.3	17	51.8
Tetrachloroethylene	9.3	30.7	76.8
Chlorobenzene	9.5	13	63.6
1,1,2-Trichloroethane	9.6	6.4	56.2
Ethylene dichloride	9.8	13	58.3
Dioxane	10.0	14	37.7
iso-Amyl alcohol	10.0	22.1	34.0
n-Octanol	10.3	11	55.0
n-Hexanol	10.7	7.6	60.0
n-Amyl alcohol	10.9	21.3	40.3
Nitroethane	11.1	17	64.8
n-Butanol	11.4	19.0	74.7
iso-Propanol	11.5	35.7	67.2
Allyl alcohol	11.8	-	80.4
n-Propanol	11.9	49.1	69.0
Benzyl alcohol	12.1	39.7	67.4
N,N-Dimethylformamide	12.1	27.9	48.9
Ethanol	12.7	58.9	71.9
Methanol	14.5	62.4	68.5
Ethanol/Water (3/1,v/v)	15.4	70.7	72.0
n-Hexane/Cyclohexane (1/1)	7.9	32.7	-
n-Hexane/Carbon tetrachloride	8.0	22.3	-
n-Octane/Carbon tetrachloride	8.1	41.8	-
Benzyl alcohol/toluene (1/1)	10.5	23.5	-
Ethanol/n-Octanol (1/1)	11.5	55.2	-
Methanol/iso-Octanol (1/1)	13.0	59.0	-
Methanol/Ethanol (1/1)	13.6	65.8	-
No Solvent	-	81.3	106

fibroin reaction catalyzed by various salts (10). The dispersion may suggest that the add-ons or the reaction rates cannot be interpreted by the solubility parameter only, but by another factor. This relationship can be estimated as follows, as in the silk-epoxide reaction. The concentration of the epoxide in the aqueous phase may have a minimum value in the case of a solvent whose solubility parameter is similar to that of the

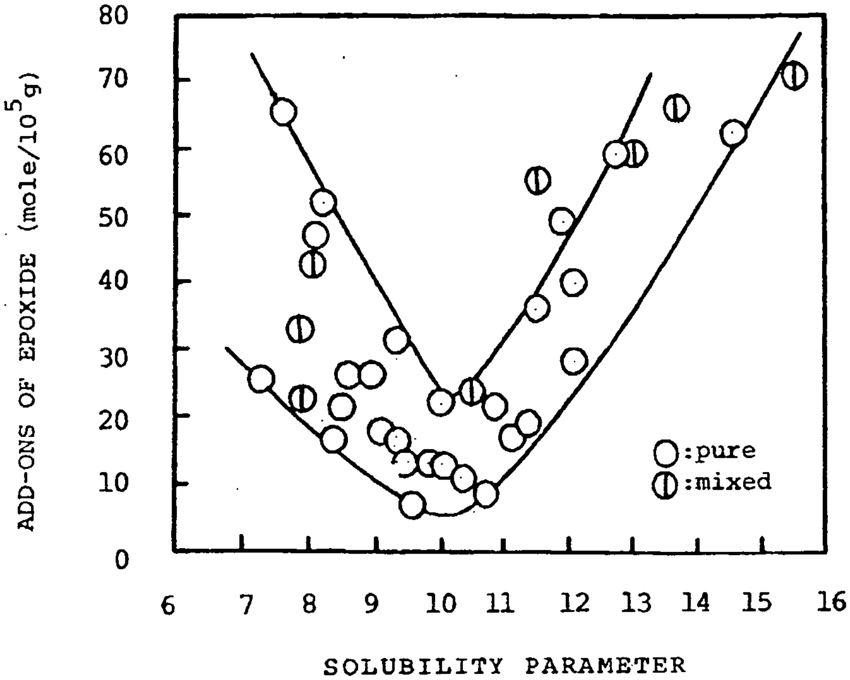

Figure 3: Solvent effect on the phenyl glycidyl ether reaction at 75°C for 3 hr without padding catalysts.

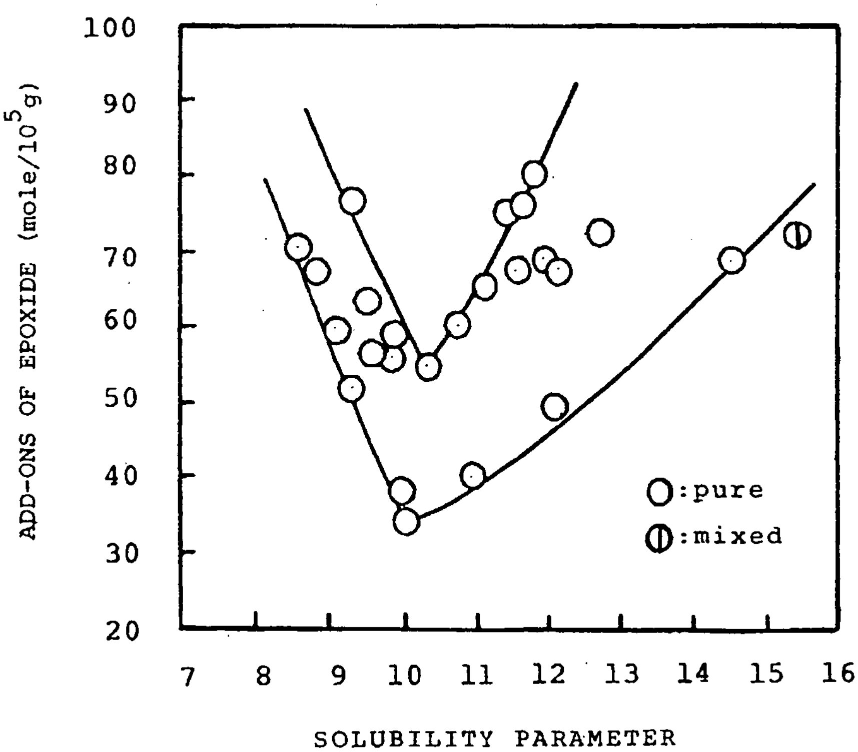

Figure 4: Solvent effect on the epichlorohydrin reaction at 68°C for 3 hr without padding catalyst.

epoxide. Therefore, the reaction rate should reach a minimum value in such the solvent, as shown in Figure 3 and Figure 4, if the epoxide in the aqueous phase can react with wool keratin and if the reaction rate depends on the concentration of epoxide. Thus, the weight gains of wool fibers decrease with increasing solubility parameter, reach a minimum value about at 10 or at the solubility parameter of a epoxide, and then increase with the parameter. Under these conditions, the swelling of the fiber seems to be similar in the solvents used.

In the reaction between wool keratin and the epoxide under the condition, three possibilities may exist: the reaction may proceed in an aqueous phase containing salt, epoxide and an organic solvent dissolved in water; in an organic phase containing salt, epoxide and water dissolved in the solvent; and at the interfaces of the aqueous and organic phases. The reactions in these cases, of course, are considered to be heterogeneous, because of the existence of the fibers. Epoxides have been found to react with various carboxylic acids, phenols, alcohols, and amines in various solvents (8), but in this case, the reaction rate decreased and approached zero as the water removed completely. Then, the reaction in organic phase can be negligible. The data of the weight gains obtained with various alcohols and ethanol-water mixture as solvents may suggest that the reaction at the interface of the aqueous and organic phases is negligibly small.

In Table I, the solubility parameter of the mixed solvent was calculated with the Scott-Magat equation (11):

$$\delta_{mix} = \Sigma V_i \delta_i$$

Here, V_i and δ_i are the volume fraction and the solubility parameter of the solvent i.

Amino acid contents of wool fibers unreacted or reacted with epichlorohydrin in various solvents at 68°C for 3 hr without padding catalysts are shown in Table II. As anticipated, the reaction of epichlorohydrin occurred very rapidly on lysine and histidine residues under these conditions. The reaction on tyrosine residues was generally rapid, while on arginine little occurred. Although the content of arginine in silk fibroin is 10 % or less of that in wool keratin, a half or more

TABLE II

Remaining Amino Acid Contents of Wool Keratin reacted with Epichlorohydrin*

Solvent	Add-ons ($mole/10^5 g$)	Remaining Amounts of Reactive Amino Acids (%)						
		His.	Lys.	Arg.	Tyr.	Cys.	Met.	Pro.
Carbon tetrachloride	70.3	0.0	12.6	89.9	56.7	73.6	58.4	85.6
Tetrachloroethylene	76.8	0.0	12.8	93.4	41.3	66.7	44.1	89.8
Methyl ethyl ketone	51.8	0.0	24.7	95.0	81.7	92.5	80.3	84.5
Chlorobenzene	63.6	0.0	16.1	92.5	69.7	79.8	64.8	84.9
Dioxane	37.7	0.0	51.6	95.8	93.2	94.2	100	98.9
n-Octanol	55.0	0.0	24.3	92.1	78.6	90.6	76.8	94.4
n-Hexanol	60.0	19.0	32.0	92.0	66.7	88.6	82.0	
n-Amyl alcohol	40.3	33.0	49.9	94.0	76.0	93.0	79.0	
Allyl alcohol	80.4	0.0	10.9	76.4	30.1	70.1	68.1	86.1
n-Propanol	69.0	0.0	16.1	86.0	49.8	85.0	77.0	
N,N-Dimethylformamide	48.9	0.0	16.1	95.1	81.3	83.6	74.9	86.9
Benzyl alcohol	67.4	0.0	23.1	89.0	61.8	87.3	73.0	
Nitroethane	64.8	0.0	37.2	91.1	96.1	95.7	95.2	86.8
n-Buthanol	74.7	0.0	12.2	85.6	40.0	76.9	71.2	88.0
Ethanol	72.0	0.0	13.8	92.1	51.4	81.7	75.2	100
Methanol	68.5	0.0	13.7	91.2	36.6	81.1	47.7	81.1

* The contents of other amino acid residues did not altered under this condition.

TABLE III

Substituent Effect of the Epoxides on the Add-ons ($mole/10^5 g$) of Wool Fiber at Indicated Temperature

Epoxide	45°C	60°C	Epoxide	45°C	60°C
Propylene oxide	20.5	43.4	n-Butylene oxide	16.0	31.1
iso-Butylene oxide	12.1	19.0	Glycidol	24.2	75.2
Epichlorohydrin	54.1	78.6	Styrene oxide	9.6	19.3
Phenyl glycidyl ether	16.7	37.7	Allyl glycidyl ether	13.3	28.0
Ethyl glycidyl ether		35.0	Glycidyl methacrylate		26.6
Glycidamide	68.6		Epibromohydrin		51.9

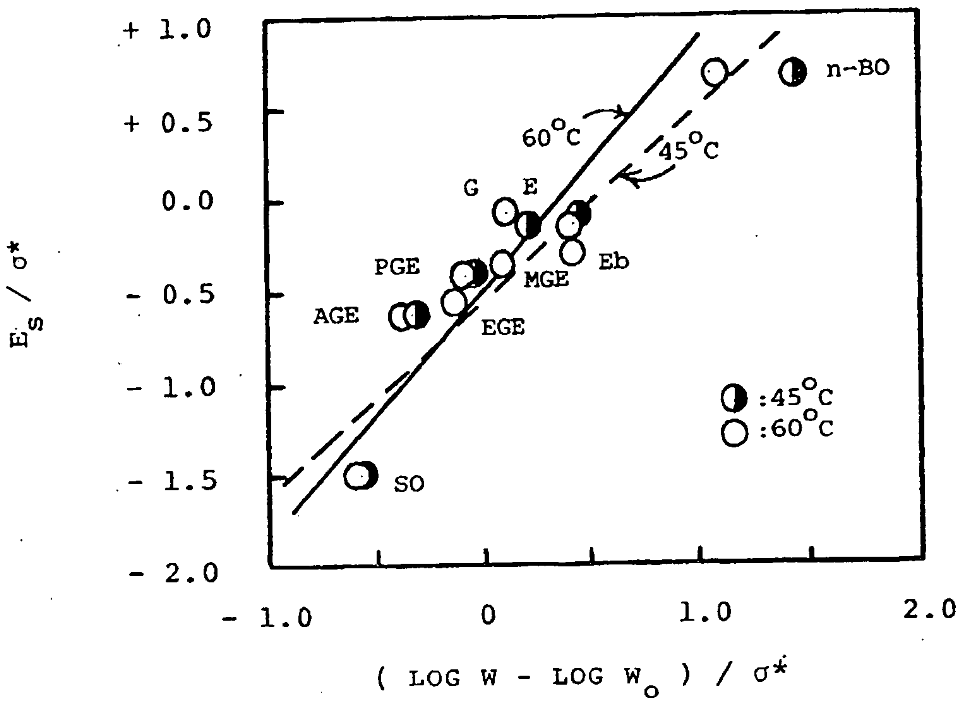

Figure 5: Substituent effect of epoxides on reaction with wool in ethanol with 0.25N $Na_2S_2O_3$-catalyst

amounts of arginine residues in the fibroin had reacted under the similar condition (7,10). No reaction occurred on serine residues, while the tyrosine reaction in wool was found to be so much as ones in the silk, especially in carbon tetrachloride, tetrachloroethylene and various alcohols but dioxane and nitroethane. The cystine content of the fiber reacted with epoxides varied noticeably with the weight gains.

The fibers padded with a 0.25N $Na_2S_2O_3$ aqueous solution were treated with a 1.43M solution of various epoxides in ethanol at the temperatures of 45 and 60°C for 3 hr. The results are summarized in Table III, and treated quantitatively with the modified Taft linear free-energy relationship (12):

$$(\log W - \log W_o) / \sigma^* = \rho_p + \rho_s E_s/\sigma^*$$

where W_o and W are the add-ons for the reaction of a given compound and for the same reaction of one of its substituted derivatives, σ^* and E_s are the polar and the steric substituent constants, and ρ_s and ρ_p are the reaction constants as measures of the susceptibility of the reaction to the polar and the steric effects of substituents, respectively.

In figure 5, $(\log W - \log W_o)/\sigma^*$ is plotted against E_s/σ^* for the reaction of a series of epoxides with wool keratin. The parent compound with the add-ons of W_o is propylene oxide, for which σ^* and E_s are both zero, and these values for other epoxides are as follows (12): n-butylene oxide, -0.100, -0.070; glycidol, 0.555, -0.177; epichlorohydrin, 1.050, -0.24; phenyl glycidyl ether, 0.850, -0.33; styrene oxide, 0.600, -0.900; ethyl glycidyl ether and allyl glycidyl ether, > 0.52, > -0.19 and < -0.33. The best straight lines have been found by the least-squares method and, from the intercept and slope, ρ_p and ρ_s are obtained as 0.39, 0.77 (45^{o}C); 0.54, 0.96 (60^{o}C), respectively. The fact that ρ_p is positive indicates that electron-withdrawing substituents increase the rate, which is usually interpreted as meaning that the reactions are S_N2. The larger ρ_s value indicates that the steric factors in the substituents play a more important role than the polar ones in these wool reactions, compared to the other epoxide reactions in solutions. The value of ρ_s/ρ_p, 1.24 - 1.38, however, is smaller than that (1.8 - 2.0) (7) for the silk fibroin reaction with the epoxide.

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